

# On the Nature of Optical Excitations in Hydrogenated Aluminium Cluster $\text{Al}_4\text{H}_6$ : A Theoretical Study

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In this paper, we present a theoretical investigation of photoabsorption spectrum of the newly synthesized hydrogenated cluster of aluminium,  $\text{Al}_4\text{H}_6$ . The calculations are performed within the wave-function-based semi-empirical method employing the complete neglect of differential overlap (CNDO) model, employing a large-scale configuration interaction (CI) methodology, and our results are found to be in very good agreement with the earlier ones obtained from the *ab initio* time-dependent density functional theory (TDDFT). We carefully analyze the many-particle wave functions of various excited states up to 8 eV, and find that they are dominated by single-particle band to band excitations. This is in sharp contrast to bare aluminium clusters, in general, and  $\text{Al}_4$ , in particular, whose optical excitations are plasmonic in nature. We attribute this difference to be a consequence of hydrogenation.

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## I. INTRODUCTION

Because of the future importance of hydrogen as a fuel, now-a-days a considerable amount of research activity is taking place in the field of hydrogen storage materials[1, 2]. This is because hydrogen is an extremely combustible gas, therefore, the preferred way to store it is in physically or chemically adsorbed forms. It is from this point of view that a large amount of theoretical and experimental research is taking place in the field of metallic hydrides. Among all possibilities, hydrides of group III elements, boron and aluminium, which are called boranes and alanes, respectively, are considered to be strong candidates for the purpose[3–5]. It is with this aim in mind, that Li *et al.*[6] recently synthesized and studied the properties of a new alane,  $\text{Al}_4\text{H}_6$ . The same group followed up this work, by performing an experimental and theoretical study of the electronic structure and properties of closo-alanes,  $\text{Al}_4\text{H}_4$ ,  $\text{Al}_n\text{H}_{n+2}$ ,  $4 \leq n \leq 8$ [7]. Besides their possible applications, alanes are of interest from a fundamental point of view as well. Boron and aluminium are in the same group of periodic table with three valence electrons each, yet their properties are very different. In the bulk form boron is a semiconductor, while aluminium is a metal. As far as the hydride chemistry is concerned, boron exhibits a huge variety of boranes with  $n$ -vertex polyhedral structures[8, 9], while the number and types of alanes is much smaller. The pioneering works of Lipscomb[10] which provide the explanations of the cage structures of boranes using the concepts of three-centered two-electron(3c-2e) bonding, ultimately resulted in an ingenious molecular orbital theory known as polyhedral skeletal electron pair theory (PSEPT) or simply Wade-Mingos rule[11–13]. On the other hand only a small number of hydrides of aluminium have

been investigated theoretically and experimentally such as molecules  $\text{AlH}$ [14–18],  $\text{AlH}_3$ [19],  $\text{Al}_2\text{H}_4$ [20]  $\text{Al}_2\text{H}_6$ [19–24], of the general type  $\text{Al}_n\text{H}_{n+2}$ [25, 26], and cage-like clusters such as  $\text{Al}_{13}\text{H}^{-m}$ [27]. Fu *et al.*[26] in a recent comparative study investigated theoretically  $\text{Al}_n\text{H}_{n+2}$  clusters, and their borane analogues. Grubisic *et al.*[7] have tried to arrive at a Wade-Mingos type of rule set for aluminium hydrides, so that their structures could be predicted in a way similar to boranes, though Martinez and Alonso[25] have recently raised doubts on this similarity. With this background in mind, the recent study of  $\text{Al}_4\text{H}_6$ ,[6] a material whose structure is consistent with Wade-Mingos rule, has again revived the analogy of aluminium hydrides with boranes. In this work we present an extensive study of the electronic structure and optical properties of  $\text{Al}_4\text{H}_6$ , with the aim of predicting its photoabsorption spectrum, and to understand the nature of its optical excitations, which can be used for optical characterization of this substance. For the purpose, we use our recently developed CNDO/INDO Hamiltonian-based semiempirical multi-reference singles-doubles configuration interaction (MRSDCI) methodology described elsewhere[28–30]. To benchmark our approach, we also apply this approach to  $\text{AlH}$  molecule and demonstrate good agreement with the experimental results. Martinez and Alonso[25] calculated the photoabsorption spectra of several alanes of the type  $\text{Al}_n\text{H}_{n+2}$  including  $\text{Al}_4\text{H}_6$ , using the *ab initio* time-dependent density functional theory (TDDFT), and our results are found to be in very good agreement with their results[25]. Upon analyzing the many-particle wave functions of the excited states corresponding to important peaks in the spectrum of  $\text{Al}_4\text{H}_6$ , we conclude that all the way up to 8 eV the states correspond to inter-band excitations, and not to plasmonic excitations common in bare Al clusters.

The remainder of this paper is organized as follows. In section II we briefly describe the theoretical methodology employed for the present calculations. This is followed by the presentation and discussion of our results in section III. Finally, in section IV we present our conclusions.

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## II. THEORY

For our study, we adopted a wave-function based electron-correlated approach employing the semi-empirical valence-electron CNDO/2 model Hamiltonian developed by Pople and coworkers[31–33]. The methodology adopted in this work is discussed in detail in our earlier papers[28–30], therefore, we present only a brief description of it here. As compared to our earlier works on boron-based clusters[29, 30] where we had used the INDO model, the choice of CNDO/2 model here has to do with the fact that INDO parameters are not available for the third row atoms like aluminium in the original Pople approach[34]. Our calculations are initiated at the Hartree-Fock (HF) level, within the CNDO/2 model, using a computer program developed recently by us[28]. The CNDO-HF molecular orbitals (MOs) thus obtained, are used to transform the Hamiltonian from the original atomic-orbital (AO) to the MO representation, which is subsequently used in the post-HF correlated calculations. The transformed CNDO/2 Hamiltonian matrix elements in the MO representation are supplied to the computer program package MELD[35], which is used to perform the correlated calculations using the multi-reference singles-doubles configuration-interaction (MRSDCI) approach. Using the ground- and excited-state wave functions obtained from the MRSDCI calculations, electric dipole matrix elements are computed and subsequently utilized to compute the linear absorption spectrum, under the electric-dipole approximation, assuming a Lorentzian line shape. By analyzing the excited states contributing to the peaks of the computed spectrum obtained from a given calculation, bigger MRSDCI calculations are performed with a larger number of reference states. This procedure is repeated until the computed spectrum converges within an acceptable tolerance. In the past, we have used such an iterative MRSDCI approach on a number of conjugated polymers to perform large-scale correlated calculations of their linear and nonlinear optical spectra[36].

## III. RESULTS AND DISCUSSION

In this section we present and discuss our results on the electronic structure and optical properties computed using our CNDO-MRSDCI approach. However, before that, to benchmark our methodology we present and discuss our CNDO-CI results on the simplest hydride of aluminium, namely AlH.

### A. AlH Molecule

First we performed the geometry optimization of the AlH molecule at the CNDO-HF level, by calculating the total energy of the system for different bond lengths, and

then locating the minimum. Our optimized bond length was found to be 1.75 Å which is 0.1 Å larger than the reported experimental value of 1.65 Å[14, 15]. However, our aim here is to compute the optically-active excited states of the molecule, and as we will show later that this much of difference in the geometry leads to insignificant differences in their excitation energies.

In the CNDO/2 model Al has nine Slater-type basis functions (1s, 3p, 5d), while H has only one basis function, leading to ten basis functions in all. Being a valence electron approach, the total number of electrons being explicitly considered for AlH within the CNDO/2 model is four, with Al contributing three electrons, and H one. Therefore, with four electrons, and ten basis functions full-CI (FCI) calculations for the system are feasible, because in the singlet subspace the total number of all possible configuration state functions (CSFs) is only 825. Thus, the FCI results presented here are exact within the chosen model (CNDO/2), and any disagreements with the experiments will indicate the deficiency of the model rather than that of the CI expansion.

The CNDO-HF calculations predict the Mulliken population of Al(H) atoms to be +0.24(-0.24), implying a partial ionic character to this system, with Al being the electron donor, fully consistent with previous works[23]. The absorption spectrum of AlH is well-known and has been studied extensively over the years both experimentally[16] and theoretically[15, 17, 18]. The ground state of the system is classified as  $X^1\Sigma^+$  while the dipole connected excited states are  $A^1\Pi$ ,  $C^1\Sigma^+$ ,  $D^1\Sigma^+$ , and  $E^1\Pi$ . The first excited state  $A^1\Pi$  corresponds to  $\text{HOMO}(H) \rightarrow \text{LUMO}(L)$  transition which is  $5\sigma \rightarrow 2\pi$  in nature. The reported experimental value of this transition is 2.91 eV, with which our calculations are in good agreement with the computed values of 3.11 eV, and 3.12 eV at the bond lengths of 1.75 Å (our optimized bond length) and 1.65 Å (experimental bond length) respectively. This also shows that small differences in geometry have negligible impact on the calculated excitation energy of the lowest excited state. The  $C$  and  $D$   $\Sigma$ -bands correspond to Rydberg-type excitations and, therefore, cannot be computed using CNDO approach, because they require the use of extremely diffused basis functions[15]. The  $E^1\Pi$  band corresponds to  $|H-1 \rightarrow L\rangle$  ( $4\sigma \rightarrow 2\pi$ ) excitation, and has been measured close to 6.9 eV[16], while our calculation predicts its value to be 7.1 eV, thus overestimating it by 0.2 eV. We note that quantitatively speaking, the disagreement between our results, and the experimental ones, both for the  $A^1\Pi$ , and  $E^1\Pi$  bands is 0.2 eV, which is quite satisfying, given the semiempirical nature of this approach. Having benchmarked the CNDO-CI approach for the case of the AlH molecule, next we present the results of our calculations for  $\text{Al}_4\text{H}_6$ .

## B. $\text{Al}_4\text{H}_6$

We first carried out the geometry optimization of  $\text{Al}_4\text{H}_6$  within a density functional theory (DFT) based approach, using Gaussian03 computational package[37] employing B3LYP functional, and 6-311+g(d) basis set. The optimized geometry is presented in Fig.1, and it is virtually identical to that reported by Li *et al.*[6] As noted by Li *et al.*[6] also, this structure is very similar to the computed structure of the borane,  $\text{B}_4\text{H}_6$ [38] which still has not been synthesized. We used this DFT optimized geometry to perform the calculations of the photoabsorption spectrum within our CNDO-CI approach, as well as the *ab initio* TDDFT method.

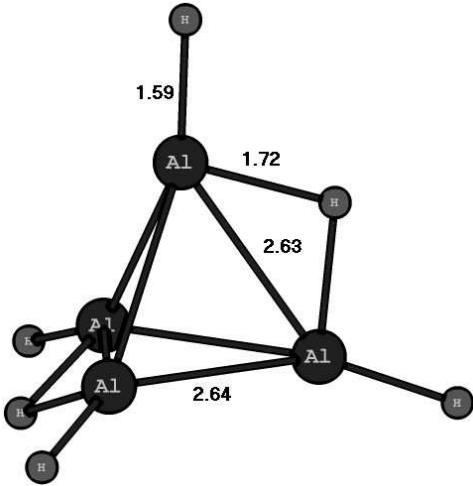


Figure 1: Optimized geometry of  $\text{Al}_4\text{H}_6$  obtained from the *ab initio* DFT calculations (see text for details). Each bond length (in Å) has also been indicated.

Before discussing our calculated spectra, we present some of the molecular orbitals (MOs) of the system close to the Fermi level. In Fig. 2 MOs obtained from the CNDO-HF calculations are presented. Although, here we have not presented the *ab initio* B3LYP MOs which were used to perform the TDDFT calculations, we note that among the occupied orbitals,  $H - 3$ ,  $H - 1$ , and  $H$  obtained from the CNDO-HF and the DFT calculations were qualitatively very similar. Mulliken charges of various atoms indicate Al to be in slightly cationic state, while the H atoms carry small negative charges. Therefore, we conclude that the bonding in the system is largely covalent, with some polar character. The covalent nature of the bonding is also obvious from the MO plots, which show that there is significant amount of charge density in the region between the atoms.

Next, we present and discuss the linear optical absorption spectrum of the system computed using the CNDO-CI and the *ab initio* TDDFT methods. The calculations were performed using the geometry shown in Fig. 1, which as mentioned above, was obtained at the

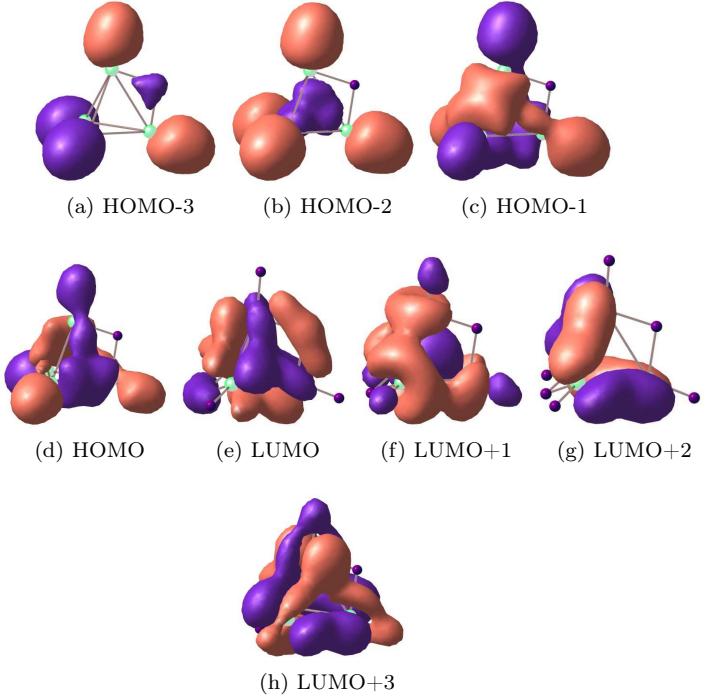


Figure 2: (Color online) Molecular orbitals (iso plots) of  $\text{Al}_4\text{H}_6$  from HOMO-3 to LUMO+3, obtained from the CNDO-HF calculations.

B3LYP/6-311+g(d) level of theory. For the CNDO-CI calculations the total number of valence electrons was 18 and the total number of basis functions was 42, thus ruling out the FCI calculations. Therefore, as mentioned in section II, the MRSDCI method was adopted to compute correlated wave functions and energies of the ground and the optically active excited states. The calculations were performed without the use of point-group symmetry, therefore, the CI expansion became fairly large scale, with the largest CI calculation consisting of 1.3 millions CSFs. The CI matrix was iteratively diagonalized[35] to obtain 60 lowest roots which required several hours of CPU time. The dipole moments connecting these excited states to the ground state were used to compute the photoabsorption spectrum presented here. Before discussing our final spectrum, in Fig. 3 we present the convergence of our optical absorption results with respect to the size of the CI matrix, represented in this case by the number of reference configurations ( $N_{\text{ref}}$ ) from which singly- and doubly- excited CSFs were generated to obtain the MRSDCI expansion. For example, in our largest MRSDCI calculation we used  $N_{\text{ref}}=22$  which generated 1.3 million total CSFs. The convergence of our calculations with respect to  $N_{\text{ref}}$  is obvious from Fig. 3, in which the spectra corresponding to  $N_{\text{ref}}=14$  and  $N_{\text{ref}}=22$  are virtually indistinguishable.

In Fig. 4, we present our final linear optical absorption spectrum of  $\text{Al}_4\text{H}_6$  computed using the CNDO-CI method. Before discussing our spectrum in detail, we

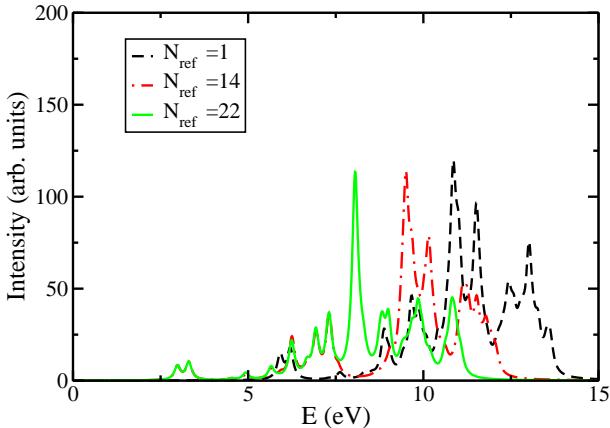


Figure 3: (Color online) Convergence of the linear absorption spectrum of  $\text{Al}_4\text{H}_6$  computed using the CNDO-MRSDCI method with respect to the number of reference states used in MRSDCI calculations. A line width of 0.1 eV was used to compute the spectra.

would like to benchmark it against other calculations to ensure its correctness. Therefore, to ascertain the accuracy of our CNDO-CI calculations, we also performed *ab initio* TDDFT calculation of its lowest photoexcited state, at the B3LYP/6-311+g(d) level of theory using the Gaussian03 program package[37]. Our CNDO-CI value of 2.98 eV (peak I in Fig. 4), compares excellently with the TDDFT value of 3.03 eV, which gives us confidence as to correctness of our calculation. Martinez and Alonso[25] used an *ab initio* TDDFT methodology to compute the photoabsorption spectrum of  $\text{Al}_4\text{H}_6$  all the way up to 12 eV (*cf.* Fig. 7 of Ref.[25]). The first peak in the TDDFT spectrum of Martinez and Alonso[25] is at an energy slightly higher than 3 eV, and their highest peak occurs at an energy close to 9 eV, thus making their spectrum slightly blue-shifted compared to ours. However, the qualitative nature of their spectrum[25] is quite similar to our spectrum discussed below.

Next, we examine the nature of excited states corresponding to the peaks present in our calculated spectrum (*cf.* Fig. 4). The important peaks in the spectrum up to the excitation energy  $\approx 8$  eV have been labeled, and the many-particle wave functions of these excited states, along with their ground-state transition dipole moments, are presented in table I. The first peak in Fig. 4 occurs at 2.98 eV, and is a relatively weak peak corresponding to the across the gap  $H \rightarrow L$  transition. The next peak (II) located at 3.28 eV is also similarly weak and corresponds to  $H - 1 \rightarrow L$  excitation. When we examine the nature of the many-particle wave functions (*cf.* Table I) of various excited states, we realize that: (a) the wave functions of all the states consist predominantly of singly-excited CSFs, (b) all the states have

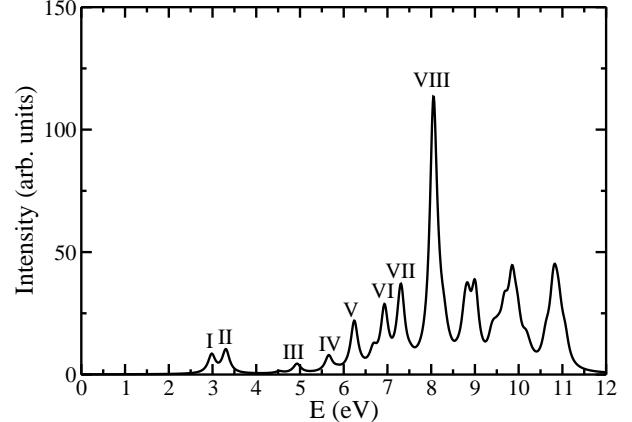


Figure 4: Linear optical absorption spectrum of  $\text{Al}_4\text{H}_6$ , computed using the CNDO-MRSDCI approach. Peaks with energies up to 8 eV have been labeled. A line width of 0.1 eV was used to compute the spectrum.

one dominant configuration with magnitude of its coefficient always greater than 0.8, with some configuration mixing with the increasing excitation energy. The highest peak in the spectrum is located at 8.05 eV with the dominant CSF being  $|H - 1 \rightarrow L + 7\rangle$ , with some contributions from  $|H \rightarrow L + 9\rangle$  and  $|H - 2 \rightarrow L + 3\rangle$ . Koutecký and coworkers[39] have formulated a criterion according to which if the many particle wave function of a given excited state is dominated by one singly-excited configuration, it is classified as a normal inter-band absorption. On the other hand, if the wave function exhibits strong mixing of several CSFs with coefficients of almost equal magnitude, it is considered to be a plasmonic collective excitation[39]. In metallic clusters such as  $\text{Al}_4\text{H}_6$ , to know whether the excited states are plasmonic in nature or not, is always of interest. As per the Koutecký [39] criterion, the excited states corresponding to peaks I to VIII do not appear to be of plasmonic type. This is to be contrasted with the nature of optical absorption in the bare  $\text{Al}_4$  rhombus cluster which were found to be of plasmonic type by Deshpande *et al.*[40] in an *ab initio* time-dependent local-density approximation (TDLDA) calculation. In their work, authors reported that low-intensity optical absorption in  $\text{Al}_4$  begins close to 1 eV, and increases in intensity with energy peaking around 8 eV. This suggests that in  $\text{Al}_4\text{H}_6$ , it is the influence of hydrogenation which increases the optical gap, as well as changes the nature of excited states from plasmonic to inter-band excitations.

#### IV. CONCLUSIONS

In conclusion, we have presented the linear optical absorption spectrum of  $\text{Al}_4\text{H}_6$  calculated using a wave function based methodology employing the CNDO-CI ap-

Table I: Excitation energies and many-particle wave functions of excited states corresponding to the peaks in the CNDO-CI linear absorption spectrum of Al<sub>4</sub>H<sub>6</sub> (*cf.* Fig. 4), along with the squares of their dipole coupling ( $\mu^2 = \sum_i |\langle f | d_i | G \rangle|^2$ ) to the ground state.  $|f\rangle$  denotes the excited state in question,  $|G\rangle$ , the ground state, and  $d_i$  is the *i*-th Cartesian component of the electric dipole operator. In the wave function column, the numbers in the parentheses are the CI coefficients of a given electronic configuration. Symbols  $H/L$  denote HOMO/LUMO orbitals.

| Peak | Energy (eV) | $\langle \mu^2 \rangle$ | Wave function                             |
|------|-------------|-------------------------|---|
| I    | 2.98        | 0.08                    | $ H \rightarrow L\rangle(0.9425)$         |
| II   | 3.28        | 0.09                    | $ H - 1 \rightarrow L\rangle(0.9423)$     |
| III  | 4.93        | 0.02                    | $ H - 1 \rightarrow L + 2\rangle(0.9226)$ |
|      |             |                         | $ H \rightarrow L + 1\rangle(0.1531)$     |
| IV   | 5.66        | 0.03                    | $ H \rightarrow L + 3\rangle(0.9313)$     |
| V    | 6.24        | 0.07                    | $ H - 1 \rightarrow L + 3\rangle(0.9027)$ |
|      |             |                         | $ H - 1 \rightarrow L + 4\rangle(0.1609)$ |
|      |             |                         | $ H \rightarrow L + 4\rangle(0.1056)$     |
| VI   | 6.93        | 0.11                    | $ H \rightarrow L + 5\rangle(0.9249)$     |
|      |             |                         | $ H \rightarrow L + 4\rangle(0.1242)$     |
| VII  | 7.31        | 0.12                    | $ H - 3 \rightarrow L\rangle(0.8391)$     |
|      |             |                         | $ H - 1 \rightarrow L + 5\rangle(0.3062)$ |
|      |             |                         | $ H - 2 \rightarrow L + 2\rangle(0.1600)$ |
| VIII | 8.05        | 0.44                    | $ H - 1 \rightarrow L + 7\rangle(0.8590)$ |
|      |             |                         | $ H \rightarrow L + 9\rangle(0.2880)$     |
|      |             |                         | $ H - 2 \rightarrow L + 3\rangle(0.1812)$ |

proach, and compared it with that computed using the *ab initio* TDDFT approach. The photoabsorption spectra computed using the two approaches are generally in good agreement with each other, with the published TDDFT spectrum[25] being slightly blue-shifted compared to our work. Therefore, it will be of considerable interest to perform optical absorption experiments on Al<sub>4</sub>H<sub>6</sub> cluster, to determine the nature of its optical excitations, and shed further light on its electronic structure. Our results can then be used for optical characterization of this cluster.

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